

# Exfoliated Layered Materials for Digital Fabrication

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## Abstract

We introduced an exfoliation method of MoS<sub>2</sub> in a 3% solution of sodium dodecyl surfactant at high concentration (i.e. 2 g/L). The bulk MoS<sub>2</sub> was thinned by mechanical exfoliation between sand papers and the resulting powder was used to prepare dispersions by liquid exfoliation through probe sonication. The resulting dispersion consisted of very thin MoS<sub>2</sub> nanosheets in surfactant solution with average lateral size around 126 nm. This may be interesting for applications in inkjet printed electronics.

## Introduction

Molybdenum disulfide, MoS<sub>2</sub> is a transitional metal dichalcogenide part of an important class of layered materials where the metal layers are sandwiched between two layers of chalcogen atoms [1]. These intralayers are held together by weak van der Waals forces whereas strong covalent forces hold the individual atomic interlayers together [2, 3].

The discovery of graphene [4] and the developments thereafter, led to the research of other layered materials which, likewise graphene, have remarkable properties at atomic scale that are explored when these materials are exfoliated into thin to atomic monolayers. Some of these properties included a sizeable band gap which is naturally occurring in MoS<sub>2</sub> and allowed the fabrication of very thin elementary physics devices such as a Field Effect Transistor which could be turned on and off due to this property. Graphene cannot be employed for that, unless an engineered bandgap is introduced into the material [5, 6]. Bulk MoS<sub>2</sub> has an indirect band gap of 1.2 eV [7] which increases up to 1.9 eV [5, 6] for monolayers exhibiting a transition to a direct band gap semiconductor [6] together with increase in photoluminescence [8, 9]. This feature was remarkable, as shifting the band gap from the near infrared to the visible range make these materials specially interesting for optoelectronics [6] such as photovoltaic applications [10].

The two most promising methods for solution processing of layered materials to date are liquid (LE) and chemical exfoliation (CE) [3].

Here we focused on LE due to its higher yields compared to CE, and even though fewer monolayers were achieved with this method, LE presented some other processing advantages as no controlled atmosphere was necessary and, no flammable and expensive materials were employed, therefore it may be the preferable route for applications where large quantities of exfoliated nanosheets are desirable such as composites, energy storage devices and catalysis applications [3].

Many of those devices could be fabricated digitally using inkjet printing or 3D printing. Inkjet printing of layered materials such as graphene and MoS<sub>2</sub> was reported earlier by Finn et al [11] using organic solvents but water based inks have advantages and can be used in most of the fastest printing heads available in the market nowadays. We therefore study the fabrication of 2D inks using the environmental friendly solution of SDS (Sodium Dodecyl Sulfate) surfactant and water to prepare the MoS<sub>2</sub> dispersions.

## Materials and methods

The MoS<sub>2</sub> (Molybdenum IV sulfide) powder (99% < 2 μm) and the surfactant SDS (Sodium Dodecyl Sulfate) were purchased from Aldrich and used as supplied.

To mechanically exfoliate the MoS<sub>2</sub> powder we used an orbital sander featuring nominal speed of 11000 rpm (Meecc Tools) and exfoliated the powder between sand papers with mesh size 1000 or higher.

The method used to exfoliate the powder and the liquid exfoliation of the dispersion were also employed by us in another study [1] except for the use of surfactant. Figure 1 illustrates the steps used during the preparation of the dispersion or 2D ink in the left side, and a picture of the dispersion shortly after centrifugation on the right side. The liquid exfoliation was performed using a Sonics Vibracell CV334, 750W probe unit. The dispersion was placed in a 100mL jacket glass vessel (Ace glass incorporated) which was connected to a pump (Polyscience 801 heat circulator) to allow the cold water at 5 °C to flow through the jacket and avoid overheating of the dispersion.

To protect the probe from overheating during the processing time (60 min), it was set to operate 8 s on and 2 s off.

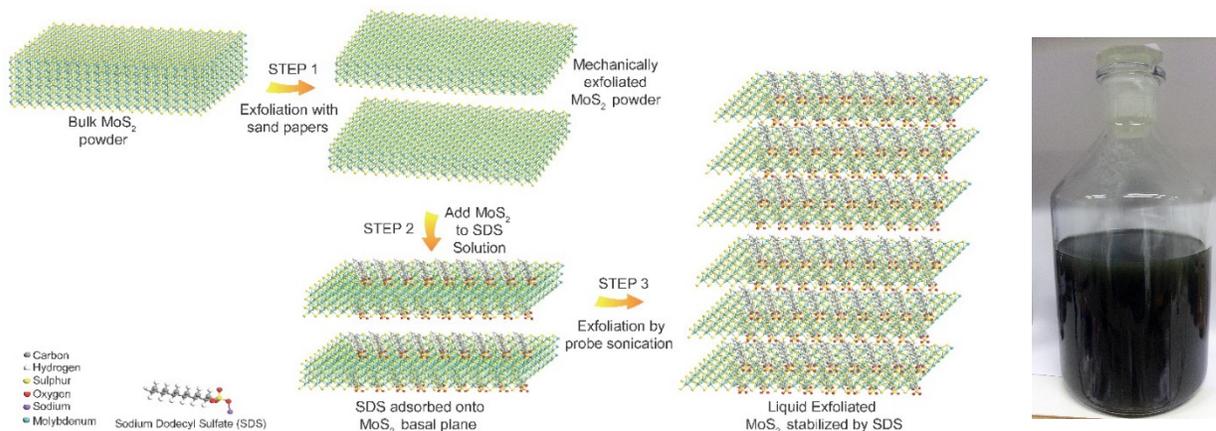


Figure 1: Exfoliation steps for the production of MoS<sub>2</sub> dispersions in the left side, and a picture of 1L liter dispersion on the right side.

AFM (Atomic force microscopy) images were made using a Dimension 3100 AFM (Digital Instruments) operated in tapping mode. The samples were centrifuged (Jouan A14) at 1500 rpm for 45 min decanted to remove non-exfoliated particles. The liquid of the remaining dispersion was removed and the nanosheets were re-dispersed in 99,5% ethanol. We then deposited drops of this dispersion onto a silicon wafer for the imaging analysis.

The stability of the dispersions was accessed using zeta potential measurements (Malvern Zetasizer Nano). The particle size distribution was evaluated using the same instrument and same sample. SEM images (Scanning electron microscopy) were made using a FEI Nova NanoSEM.

Surface Tension measurements were carried out using the Wilhelm plate method in a Kruss K20 tensiometer.

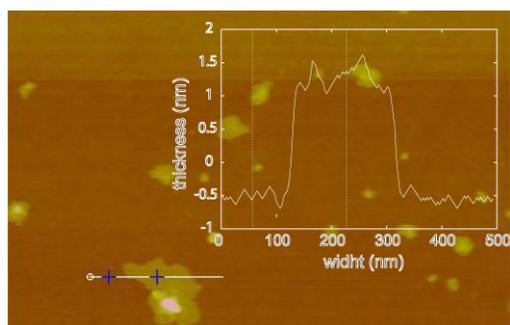


Figure 2: AFM image of nanosheets with thickness profile in the inset.

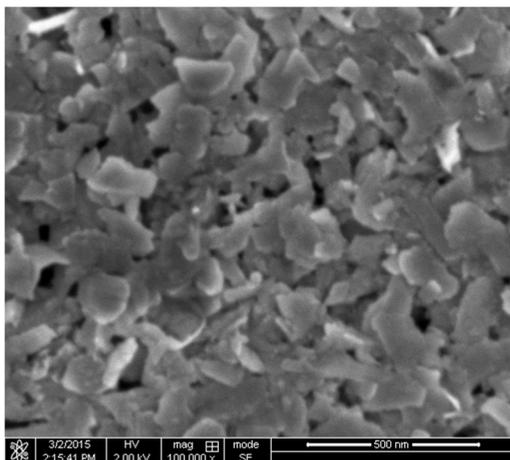


Figure 3: SEM image of the dispersion deposited onto a nitrocellulose membrane by vacuum filtration

## Results and Discussion

After exfoliation the particle size distribution of the nanosheets alters significantly as during sonication besides separating the layers of the materials some sonication scission occurs [12]. The initial range of the particles before exfoliation was around 3  $\mu\text{m}$  [1] and was reduced to about  $126 \pm 57.8$  nm according to particle size distribution measurements. We observe thin nanosheets as can be seen from the AFM image illustrated in Figure 2 with thickness of approximately 1.5 nm indicating up to two atomic layers of MoS<sub>2</sub> [13]. Figure 3 illustrates a SEM image of the nanosheets deposited by vacuum filtration.

To be able to print the dispersions and avoid clogging of the printing head nozzles it is important that the particles size of the nanosheets fall in a certain range (around 170 nm [11]), the dispersions are stable and have a lower surface tension ( $< 30$  mN/m) conditions that were observed for the dispersions prepared by the method presented here. The surface tension for the SDS dispersion in 1% stock dispersion was 28 mN/m.

We estimated the stability of the dispersion by zeta potential measurements. We measured a higher zeta potential for the dispersions using SDS than the ones in pure water [1]. For the dispersions in SDS the zeta potential was  $-39 \pm 2.3$  mV meaning that the dispersion was stable as  $\zeta > |25|$  mV [14]. This measurement was done around 6 months after the sample preparation. The mechanism of stabilization can be explained by the DLVO and Hamaker theory [15].

When we exfoliate the particles a higher surface area is available for the interactions with the surfactants. Higher surface area means higher amount of surfactant necessary to minimize flocculation in order to achieve better stability of the dispersion.

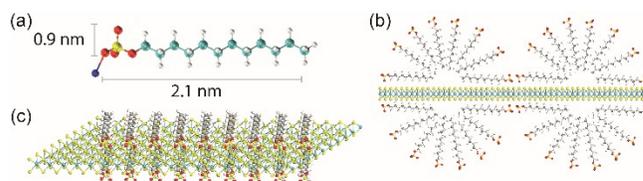


Figure 4: Mechanisms of surfactant adhesion onto the basal plane of MoS<sub>2</sub> (a) SDS molecule (b) semi-micelle adsorption mechanism (c) simplified adhesion illustration for Figure 1.

The addition of anionic surfactants such as SDS, improves the stability of dispersions through electrostatic interactions between the exfoliated particles and the surfactant, thus higher concentration is achieved [16]. The surfactant adhere to the surface of the particles and avoid agglomeration and in this way higher concentrations were achieved compared to dispersions in water only [1].

Manne and Gaub [17] suggested the mechanism of a semi-micelle adsorption onto the MoS<sub>2</sub> basal plane after some studies using the AFM technique as it is illustrated in Figure 4 (b). To simplify the mechanism of sample preparation illustration (Figure 1) we illustrated this adhesion as in Figure 4 (c).

The stock SDS solution concentration (1 g L<sup>-1</sup>) was half of the critical micelle concentration (CMC) for a pure SDS solution i.e. 8mmol L<sup>-1</sup> or 2 g L<sup>-1</sup> [18]. Lotya et al. [14] state that rising the surfactant concentration around the CMC increases the dispersion concentration (other authors say that stock concentrations much above the CMC are ideal). To test that, we dispersed MoS<sub>2</sub> in 3% stock solution and observed a tenfold increase in concentration. We measured the concentration of the prepared dispersions by drying a known amount of dispersion in an oven and subtracted the SDS concentration. This was done after centrifuging at 1500 rpm and decant the dispersions. The achieved concentration was 0.2 mg/mL for the dispersion in 1% SDS and, 2 mg/mL for the one in 3% stock solution. Even though there may be an optimal amount of surfactant for best stabilization and highest concentration, a compromise need to be taken as minimum amount of surfactant is desired to not impact some applications [19].

We performed other studies about exfoliation of layered materials in pure water without surfactants [1] but it prove to be

difficult to inkjet these dispersions due to the high surface tension but with the addition of surfactants we could jet the dispersion but we did not print a pattern by the time we wrote this manuscript. We used a Konica Minolta KM512 printing head for these tests.

## Conclusion

Here we presented a method to achieve a 2D ink containing very thin nanosheets at relatively high concentrations using MoS<sub>2</sub> in a SDS surfactant solution that could be further developed in order to be used in high speed printing heads for digital fabrication. The dispersion was stable and contained very thin nanosheets.

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